6-1964

A proposed method of separation and analysis of the Au(CN)2 and Au(CN)4 complexes

Richard Edward Beane
Union College - Schenectady, NY

A PROPOSED METHOD OF SEPARATION AND ANALYSIS OF THE $Au(CN)_2^-$ AND $Au(CN)_4^-$ COMPLEXES

by

Richard Edward Beane III

Senior Thesis Submitted
in Partial Fulfillment
of the Requirements of Graduation

DEPARTMENT OF CHEMISTRY
UNION COLLEGE

MAY 1964

This Thesis

Submitted by

Richard E Beane

to the

Department of Chemistry of Union College

in partial fulfillment of the requirements of the degree of

Bachelor of Science with a Major in Chemistry

is approved by

C J Wenck

Table of Contents

List of Figures

Introduction and Background

Due to its relative scarcity, gold has always held a high value to civilizations compared to other metals which are more common and easier to obtain. Various methods of extraction of the metal have been used throughout history, the most successful of which are washing and dissolution. The most important method of recovery at the present time is dissolution by cyanidation.

In 1783 K.W. Scheele published his findings on the solubility of gold in an aqueous solution of an alkali cyanide. The reaction for this process is:

$$2Au + 4CN^- + \tfrac{1}{2}O_2 + H_2O \longrightarrow 2Au(CN)_2^- + 2OH^-$$

The importance of oxygen in this process was recognized in 1846.

The Au^{+1} ion is non-existent in aqueous solution, oxidizing itself to Au^{+3}:

$$Au^0 \rightleftharpoons Au^{+1} + e^- \qquad -1.68 \text{ volts}$$

$$Au^{+1} \rightleftharpoons Au^{+3} + 2e^- \qquad -1.29 \text{ volts}$$

$$Au^0 \rightleftharpoons Au^{+3} + 3e^- \qquad -1.50 \text{ volts}$$

In order to stabilize Au^{+1} in aqueous solution, it is necessary to form a complex, such as the $Au(CN)_2^-$ complex which is formed in the cyanidation process. This ion is quite

stable as is evident from its dissociation constant:

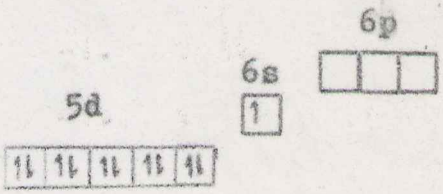
$$\frac{Au^{+} \quad CN^{-} \ ^{2}}{Au(CN)_2^{-}} = 2.5 \times 10^{-29}$$

The Au^{+3} ion is also non-existent in aqueous solution, so it too must be complexed. Such a complex is $Au(CN)_4^{-}$ which has no published dissociation constant. Since oxygen is not able to appreciably oxidize gold beyond the Au^{+1} state, the $Au(CN)_4^{-}$ complex does not appear in the cyanidation process.

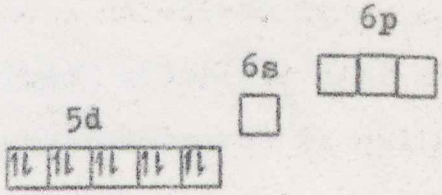
The existence of an Au^{+2} oxidation state has been suggested as in AuS. The black color of this compound, however, points to the fact that it is probably a mixture of Au_2S_3 and Au_2S. This is supported by the fact that solid $CsAuCl_3$ is diamagnetic and is actually $Cs_2Au^{1}Au^{3}Cl_6$.(4) There is, however, evidence for an Au^{+5} oxidation state in strong basic solution (pH 11.6).(5)

The electronic structures of gold in the ground state and the Au^{+1} and Au^{+3} oxidation states are:

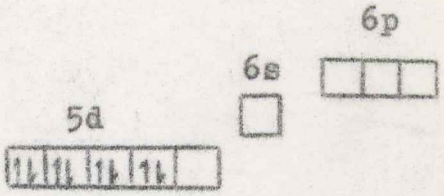
Au^{0} core to $4f^{14}\ 5d^{10}\ 6s^{1}$



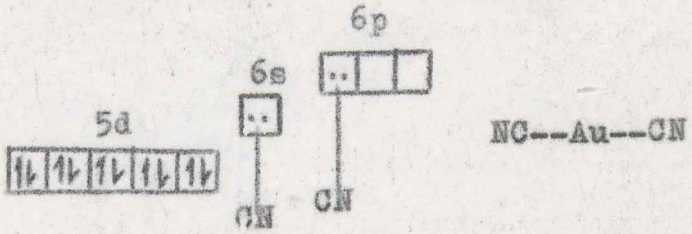
Au^{+1} core to $4f^{14}\ 5d^{10}$



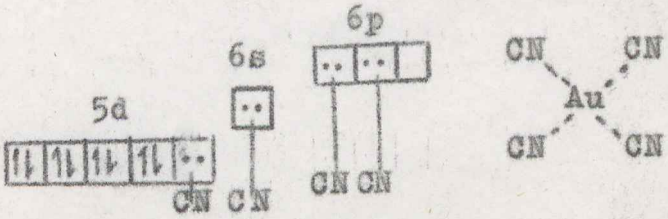
Au^{+3} core to $4f^{14}\ 5d^{8}$



The $Au(CN)_2^-$ complex is a linear molecule with the carbon of the cyanide ion bonded to the gold. The manner in which this complexing occurs is by sp hybridization:



The $Au(CN)_4^-$ complex is a planar molecule with the four gold-carbon bonds directed toward the four corners of a square. The bonding is by dsp^2 hybridization.



When the $Fe(CN)_6^-$ and $Fe(CN)_6^-$ complexes are placed in aqueous solution together, there is 100% electron transfer between the two ions.[2] It was concluded that this was aided by the high electron density around the central atom because the nitrogen atoms, which are outermost in the complex structure, bear a negative formal charge. Since the gold cyanide complexes are similar in structure to the iron

complexes, it might be expected that they might react in a similar manner.

In order to study the electron exchange between the $Au(CN)_2^-$ and $Au(CN)_4^-$ complexes, it must be possible to obtain both separately, mix them together in solution, separate them once again, and distinguish between the two complexes to determine the degree of separation. The $Au(CN)_2^-$ complex is available as the potassium salt, but the $Au(CN)_4^-$ must be synthesized from $HAuCl_4 \cdot 3H_2O$ by a modification of the method adopted from Wogrinz by Hartwell.[6]

Experimental Procedures and Results

Preparation of $KAu(CN)_4$

In a minimum amount of water, 75 grains (7.72 grams) of $HAuCl_4 \cdot 3H_2O$ were dissolved in a 50 ml. round-bottom flask. This compound is very hydroscopic and cannot be weighed accurately, but since it is available in predetermined weights in sealed vials, weighing was not necessary. The procedure proposed by Hartwell was based upon the weight of potassium cyanide present because the chlorauric acid could not be weighed accurately, but since the weight of the acid was available, it was possible to base the weights of reactants upon the amount of gold present. The reaction for the process is:

$$HAuCl_4 + 5KCN \longrightarrow KAu(CN)_4 + 4KCl + HCN\uparrow$$

weight of $HAuCl_4 \cdot 3H_2O$ used	7.72 gms. MW=394.88
weight of $HAuCl_4$ present	6.64 gms. MW=339.92
weight of KCN necessary	6.36 gms. (slight excess)

The KCN was dissolved in 25 ml. of water in a 100 ml. Erlenmeyer flask, and added in small portions to the chlorauric acid solution under a hood with constant stirring. During the exothermic reaction which followed, the color of the mixture changed from gold to yellow and finally to a colorless solution. The disappearance of color accom-

panied the transition of $HAuCl_4$ to $KAu(CN)_4$. As more $HAuCl_4$ reacted, and more $KAu(CN)_4$ was formed, the color became lighter. After all the KCN had been added, the flask was left under a hood for an hour at room temperature (24.9°C), to allow the reaction to go to completion and all the HCN to be removed. The flask was then suspended for 48 hours in a 15°C water bath, during which the $KAu(CN)_4$ precipitated in pale yellow leaflets, leaving the KCl in solution.

The mother liquor was decanted off and the crystals were redissolved in a minimum amount of boiling water. This was then filtered through charcoal to remove impurities and a second crystallization was allowed to proceed. The leaflets of $KAu(CN)_4$ now appeared colorless due to the removal of minute amounts of gold which had been reduced in the initial crystallization.

Spectral Analysis of the Complexes

Infrared spectrographic detection of the two complexes was previously impossible due to the solubility of the NaCl cells with aqueous solutions. With the availability of Irtran 2 cells, it was thought that the complexes might be analized with IR. Working with aqueous smears of the two complexes, separate absorption peaks were found for $Au(CN)_2^-$ and $Au(CN)_4^-$ at 2140 cm^{-1} and 2190 cm^{-1} respectively (Fig.1). Similar curves were found with dioxane smears, but when a

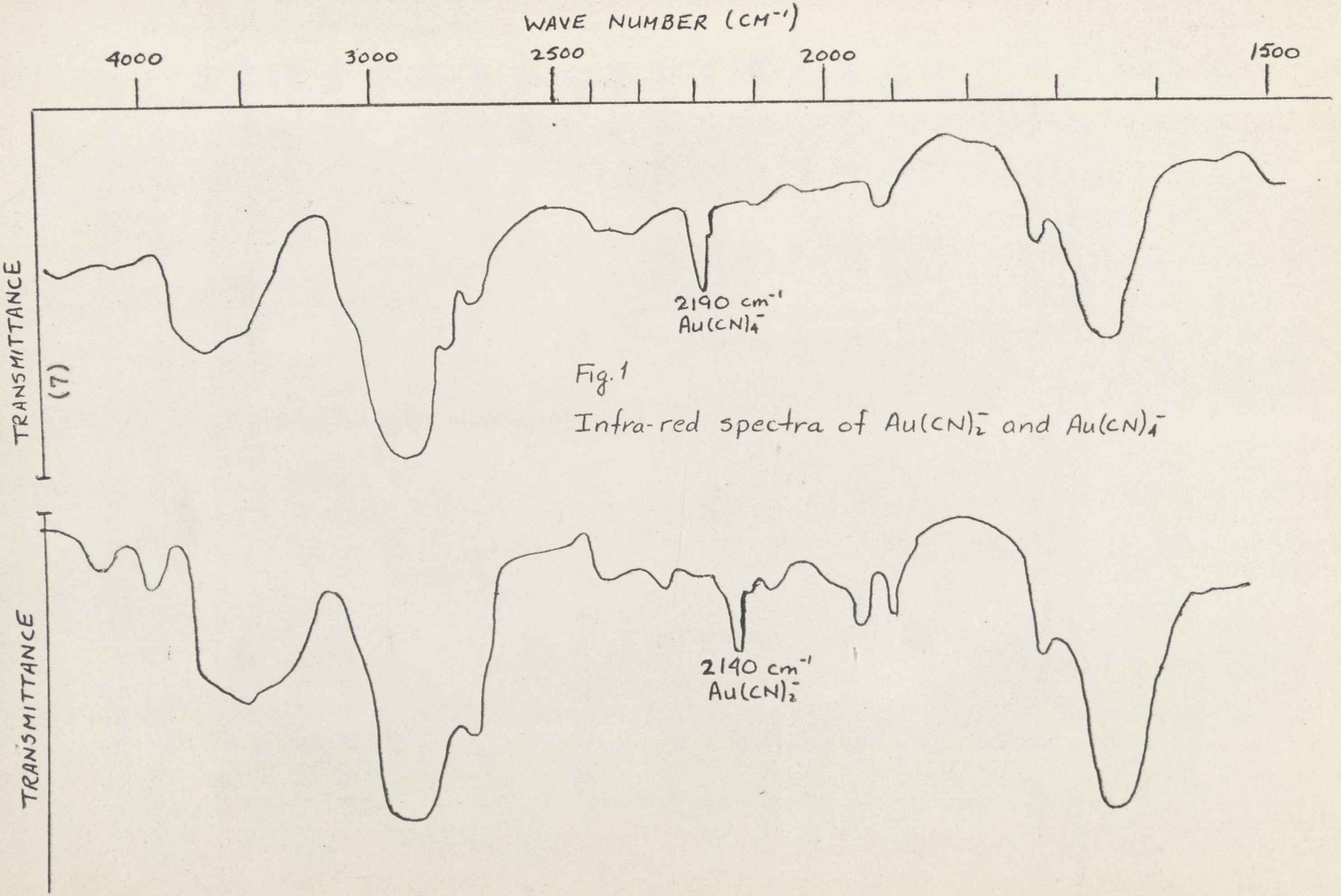


Fig. 1

Infra-red spectra of $Au(CN)_2^-$ and $Au(CN)_4^-$

dioxane-water mixture was used with the complexes in solution there were no peaks. It was then realized that IR will not detect concentrations of less than 10^{-2} molar.

Aqueous solutions of the complexes were then tested on the Beckmann DU spectrophotometer in the ultra-violet between 214 mu and 245 mu. As can be seen in Figure 2, peaks occur for the $Au(CN)_2^-$ complex around 230 mu and 239.5 mu in aqueous solution, and there are no significant peaks for $Au(CN)_4^-$ at these wavelengths (Fig.3). There is, however, a small shoulder which appears at 239.5 mu in the $Au(CN)_4^-$ solution after it has been allowed to stand for a period of time. At concentrations lower than 10^{-3} molar, the $Au(CN)_4^-$ does not appear at all at wavelengths greater than 238 mu.

When a mixture of $Au(CN)_4^-$ - water - HCl - dioxane was made up in the proportions suggested by Hartwell, there was an immediate separation of two layers. After standing for 48 hours, the bottom layer assumed a distinct yellow color. The same thing happened when the $Au(CN)_2^-$ complex was mixed in the same proportions. The concentration of both complexes before mixing was 1.0×10^{-2} molar. This separation only occurred when the HCl was present in the mix ture.

After mixing similar amounts of water - HCl - dioxane continuous spectra of the two layers of the mixture con-

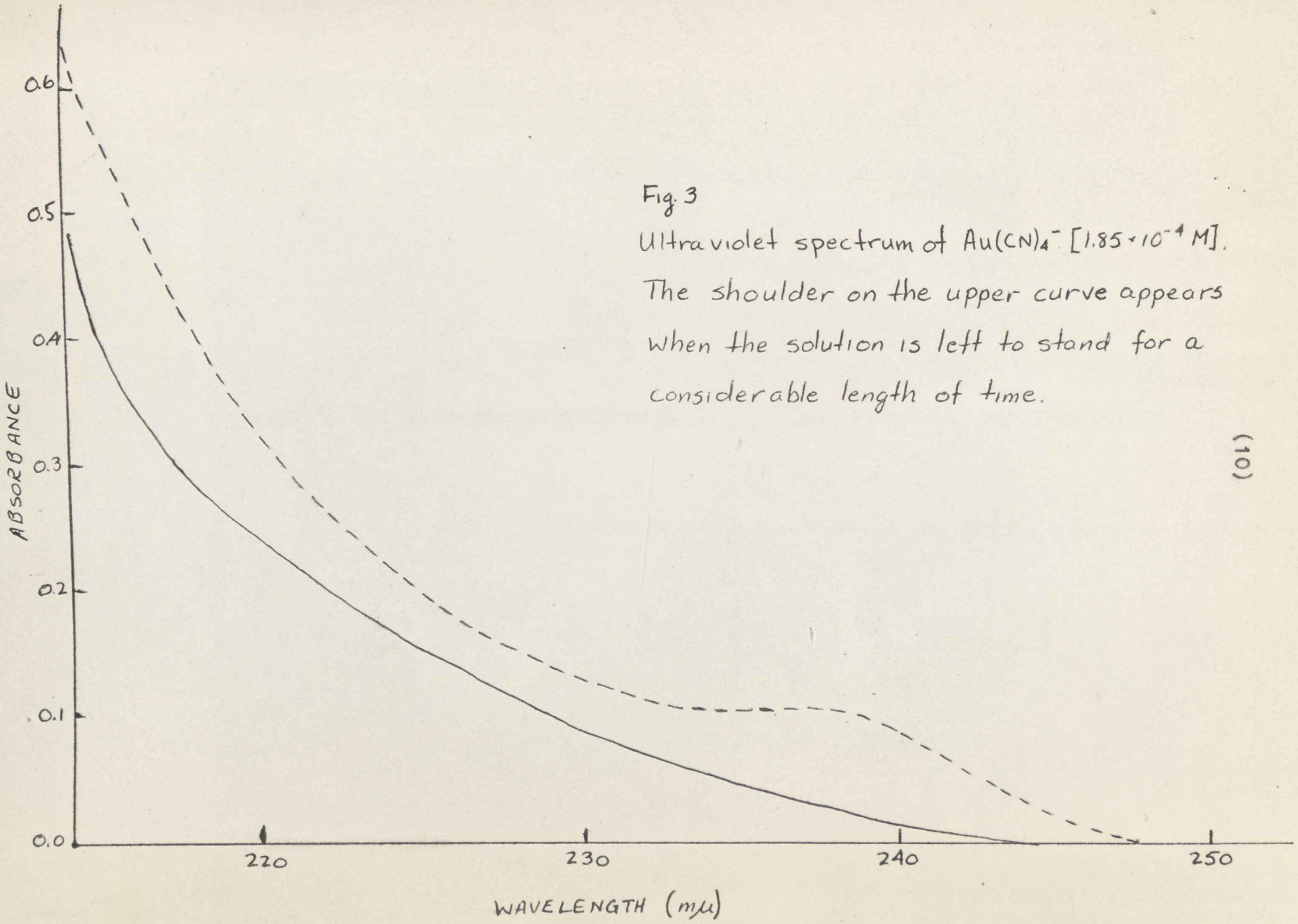


Fig. 3

Ultraviolet spectrum of $Au(CN)_4^-$ [1.85×10^{-4} M]. The shoulder on the upper curve appears when the solution is left to stand for a considerable length of time.

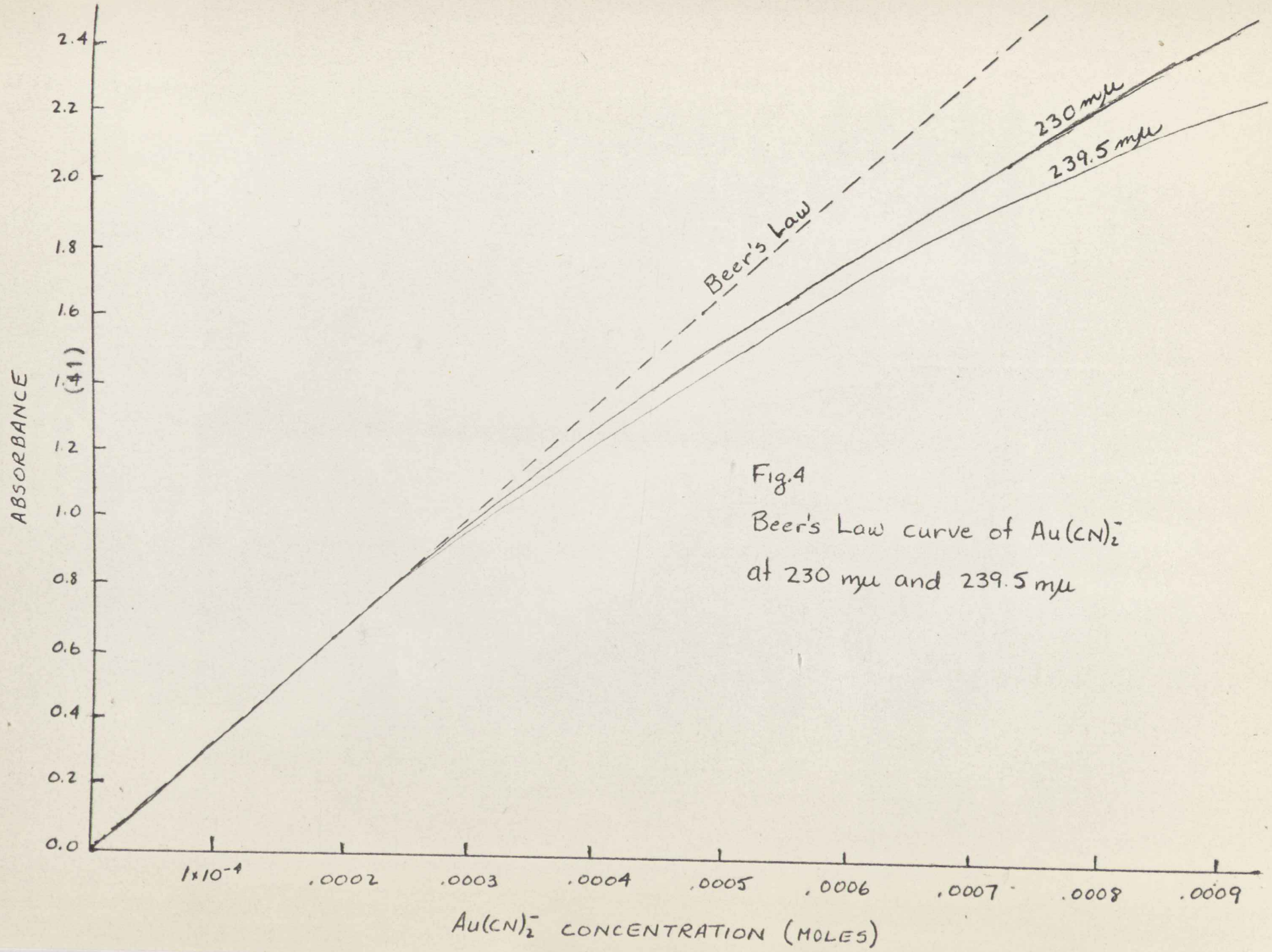


Fig.4

Beer's Law curve of $Au(CN)_2^-$ at 230 mμ and 239.5 mμ

taining the $Au(CN)_2^-$ were run against the mixture made with water as a standard. Both layers gave low absorbance until the wavelength was over 250 mu, and then they rose sharply and went off scale. The curve of the top layer (Fig.5) comes back down rapidly after reaching the peak, but that of the bottom layer descends rather slowly (Fig.6). When the bottom layer of the standard was run against water, the absorbance remained high (Fig.7).

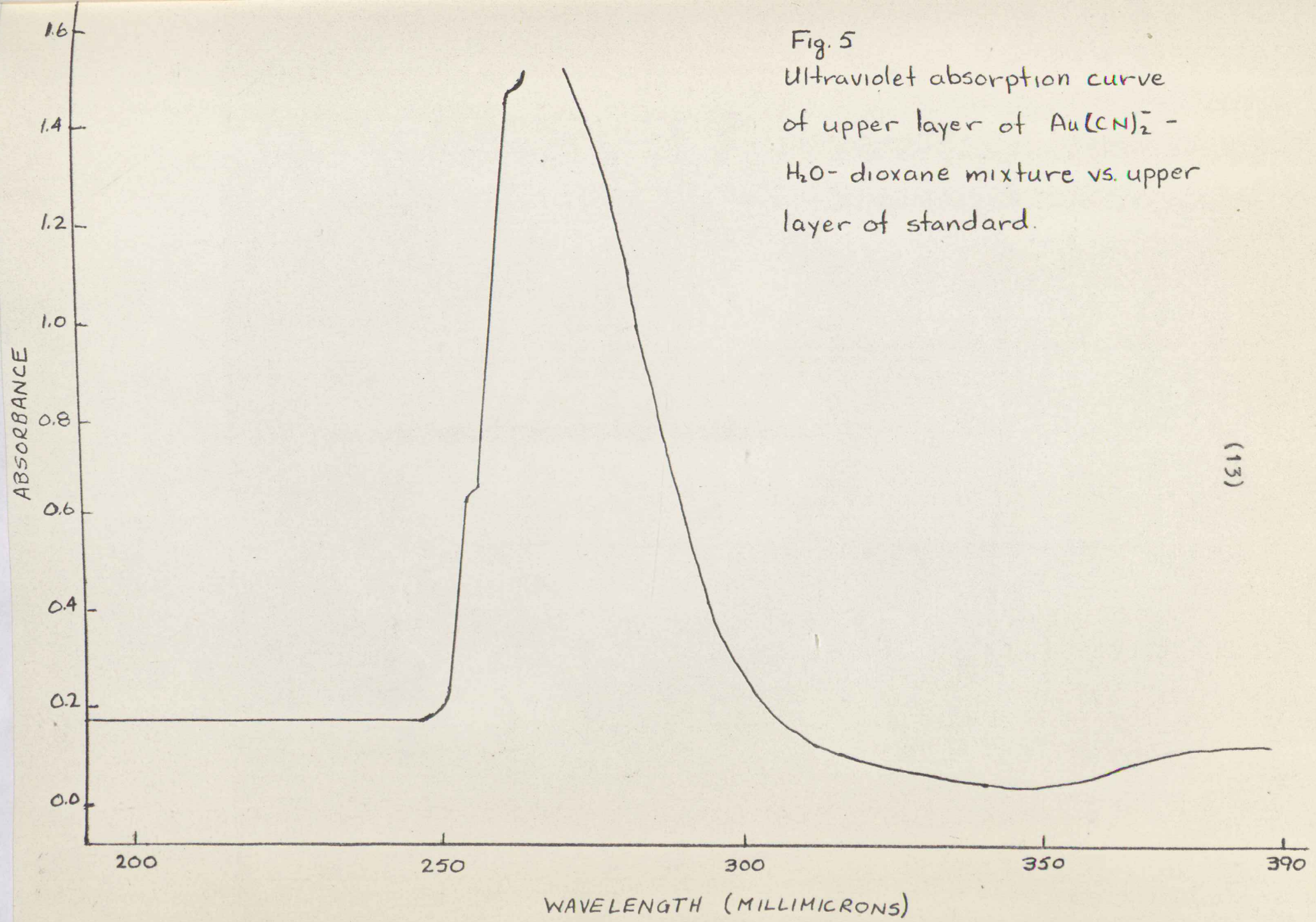


Fig. 5
Ultraviolet absorption curve of upper layer of $Au(CN)_2^-$ - H_2O - dioxane mixture vs. upper layer of standard.

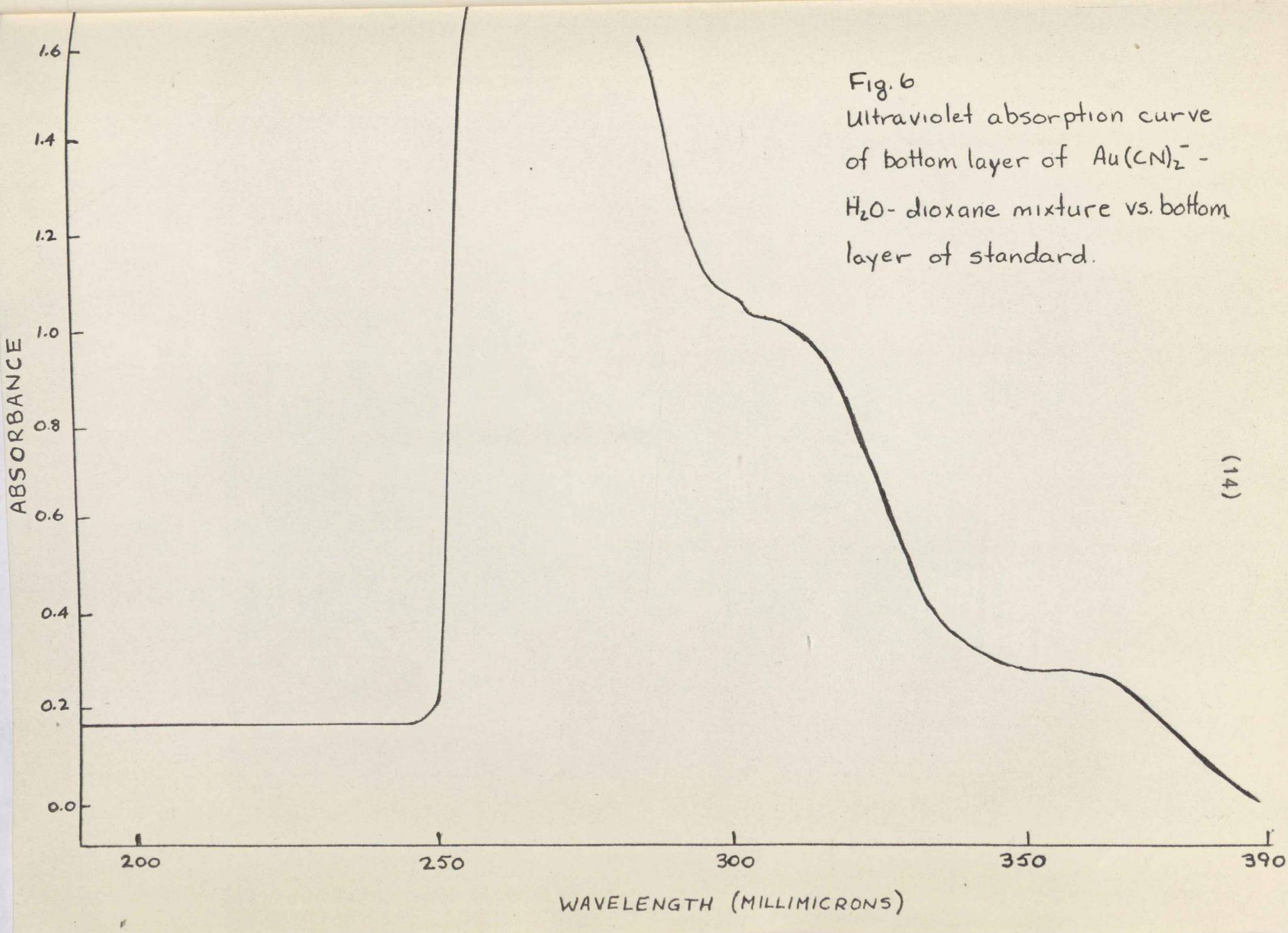


Fig. 6
Ultraviolet absorption curve of bottom layer of $Au(CN)_2^-$ - H_2O - dioxane mixture vs. bottom layer of standard.

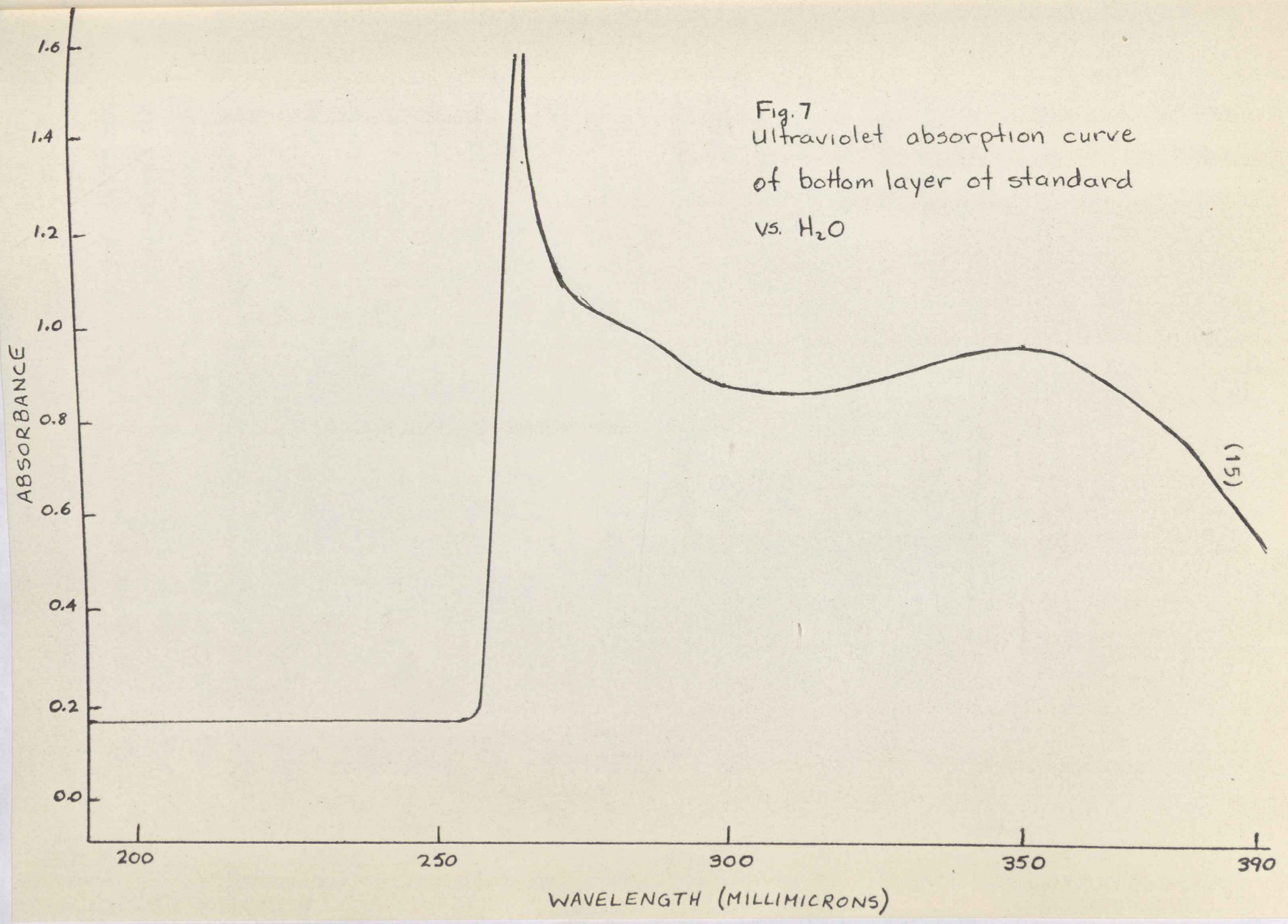


Fig. 7
Ultraviolet absorption curve of bottom layer of standard vs. H_2O

Conclusions and Discussion

Separation and Determination of the Complexes

The $Au(CN)_2^-$ complex can be detected in the ultraviolet, and if it is found to obey Beer's Law, it can be determined quantitatively. Since the $KAu(CN)_4$ does not appear at concentrations lower than 10^{-3} molar, solutions of $KAu(CN)_2$ from 10^{-4} to 10^{-3} molar were made in increments of 0.0001 and a curve of negative deviation was obtained at the two characteristic peaks of 230 mu and 239.5 mu, meaning this method can be used for quantitative determination of the $Au(CN)_2^-$ in solution (Fig.4).

Amberlite IRA 400 is a strong base-quaternary amine type resin which has a high affinity for complex cyanides. Hartwell[6] suggested that this resin be used on an ion exchange column for the separation of the $Au(CN)_2^-$ and $Au(CN)_4^-$ complexes. He bases his procedure on a paper by Aveston, Everest, and Wells[1] in which they investigated the adsorbtion of base-metal complex cyanides by the IRA 400 resin, particularly the selective adsorbtion of $Au(CN)_2^-$ from a solution of base-metal cyanide complexes.

The adsorbtion of the anions is a function of their charge, polarizability, and shape in order of decreasing importance. The $Au(CN)_2^-$ ion is held more strongly than the multivalent anions because it is a linear molecule. The major axis of polarizability of a linear ion is along

its length, and the polarization forces are concentrated in this direction. This means that the charge can be strongly directed toward the charge centers on the resin. The $Au(CN)_4^-$ complex is square planar, so the polarization forces are more dispersed and symmetrical. For this reason the $Au(CN)_2^-$ ion should be held more strongly than the $Au(CN)_4^-$ ion even though their charges are the same, because they differ in the other two factors governing adsorbtion. The suggested elutriant for the column is either an organic solvent-mineral acid mixture, or an aqueous solution of thiocyanate or perchlorate ions. The thiocyanate and perchlorate ions both have higher reduction potentials than the $Au(CN)_2^-$ ion so they would reduce the complex, and are, therefore, not able to be used as elutriants.

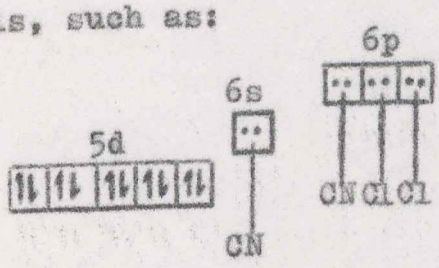
Since the ultra-violet method of analysis was to be used for solutions of either complex, it was necessary to have an organic solvent which had a cut-off wavelength lower than that of the characteristic wavelengths of the $Au(CN)_2^-$ ion, namely 230 mu and 239.5 mu. Acetone - HCl was the elutriant suggested by Aveston, Everest, and Wells, but acetone does not have the required cut-off wavelength. An alternate organic solvent is dioxane which has its cut-off around 200 mu. Hartwell suggested the use of HCl as the mineral acid in the elutriant in a ratio of

90:5:5 for dioxane : HCl : complex.

Separation in the complex - HCl - dioxane mixtures

If the $Au(CN)_2^-$ complex remained intact, then its characteristic peak would appear somewhere around 237 mu in either the top or the bottom layer, and the rest of the spectrum should go back down to low absorbance. This does not happen, however, so there is a new compound or complex being formed. This is also evident from the change in color in the bottom layer from colorless to yellow. Since the peaks occur in both the upper and lower layer layers, the reaction is affecting the composition of both layers.

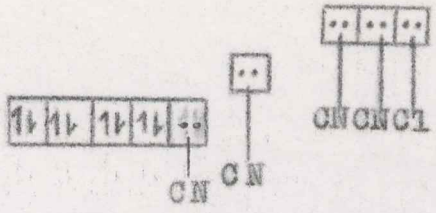
The $Au(CN)_2^-$ has two 6p orbitals available for further complexing. It is possible that there is a mixed complex being formed with the chloride ions and the two vacant orbitals, such as:



with $2Cl^-$

This structure would give an $Au(CN)_2Cl_2^{-3}$ ion having sp^3 bonding and tetrahedral structure.

Since the bottom layer was yellow in both the $Au(CN)_2^-$ and $Au(CN)_4^-$ mixtures, there must also be a feasible structure for the Au^{+3} complex in the presence of excess chloride ion. The most likely structure would be:



with $1Cl^-$

giving the $Au(CN)_4Cl^{-2}$ complex having dsp^3 bonding and trigonal bipyramidal structure.

Summary

Since it is possible to determine the amount of $Au(CN)_2^-$ in solution, the degree of separation of the two complexes on a fractionating column is able to be obtained. The quantitative presence of $Au(CN)_2^-$ in the sample can be obtained with the 237 mu wavelength if dioxane is used as the elutriant. If no $Au(CN)_2^-$ is found to be present, a wavelength of about 225 mu can be used to determine qualitatively if any $Au(CN)_4^-$ is present.

The determination of any $Au(CN)_4^-$ in the presence of $Au(CN)_2^-$ presents more of a problem. This can be surpassed, however, because quantitative peaks exist for the $Au(CN)_2^-$ complex at both 230 mu and 237 mu. Since the $Au(CN)_4^-$ present would be included in the 230 mu absorbtion peak, but not in the 237 mu peak, the quantitative determination of $Au(CN)_2^-$ would have to be the same for both peaks. If the 230 mu peak showed more $Au(CN)_2^-$ present than the 237 mu peak, it would mean that there is some $Au(CN)_4^-$ present, adding to the adsorbtion by the $Au(CN)_2^-$.

The next step is being able to observe an exchange of electrons between the two complexes. The $HAuCl_4 \cdot 3H_2O$ which is used to prepare the $KAu(CN)_4^-$ can be obtained in radioactive form as $HAu^{198}Cl_4$ with a half-life of 2.7 days. If the $Au(CN)_4^-$ is radioactively labeled when placed in solution with the $Au(CN)_2^-$, a transition of the form:

$$Au^{*}(CN)_4^- + Au(CN)_2^- \rightleftharpoons Au(CN)_4^- + Au^{*}(CN)_4^-$$

would indicate an exchange of electrons and ligands between the two complexes. This means that if the sample from the fractionating column containing maximum $Au(CN)_2^-$ and no $Au(CN)_4^-$ shows radioactivity, there has been a transition of the above form.

The main problem left is finding an elutriant which does not react with the complexes. Aveston, Everest, and Wells[5] only mention the use of HCl when used with chloride complexes. If a more dilute solution of HCl, perhaps of the order of the concentration of the complex, still gives a separation of layers with dioxane, or an eventual yellow color in the solutions, a new elutriant must be used. If chloride ion produces better separation of the chloride complexes, cyanide ion might produce the same effect with cyanide complexes. Another process might be to use hydroxide ion with a weak base-quaternary amine type resin, which actually has better displacement of multivalent by univalent complexes than with a strong base resin with chloride ion.

Bibliography

1. Aveston, J., Everest, D.A., and Wells, R.A., J. American Chem. Soc., 1958, pp. 231-9.

2. Cobble, J.W., and Adamson, A.E., J. American Chem. Soc., 1950, p. 2276.

3. Day, M.C., and Selbin, J., Theoretical Inorganic Chemistry, Reinhold Publishing Corp., N.Y., 1962.

4. Elliot, N., J. Chem. Physics, 1934, p. 419.

5. Finsen, P.O., and Murray, K.A., J. Soc. African Chem. Inst., 1960, p. 145-56.

6. Hartwell, G.E., The Synthesis and Analysis of $KAu(CN)_4 \cdot 3/2H_2O$, Union College Thesis, 1962.

7. Jones, L.H., Penneman, R.A., and Startizky, E., J. American Chem. Soc., 1956, p. 62.

8. Ricci, J.E., The Phase Rule and Heterogeneous Equilibrium, D. Van Nostrand Co., N.Y., 1951.

9. Schwartz, R., The Chemistry of Inorganic Complex Compounds, John Wiley and Sons, N.Y., 1923.

10. Sneed, M.C., Maynard, M.L., and Brastard, R.C., Comprehensive Inorganic Chemistry, Vol. II, D. Van Nostrand Co., N.Y., 1954.

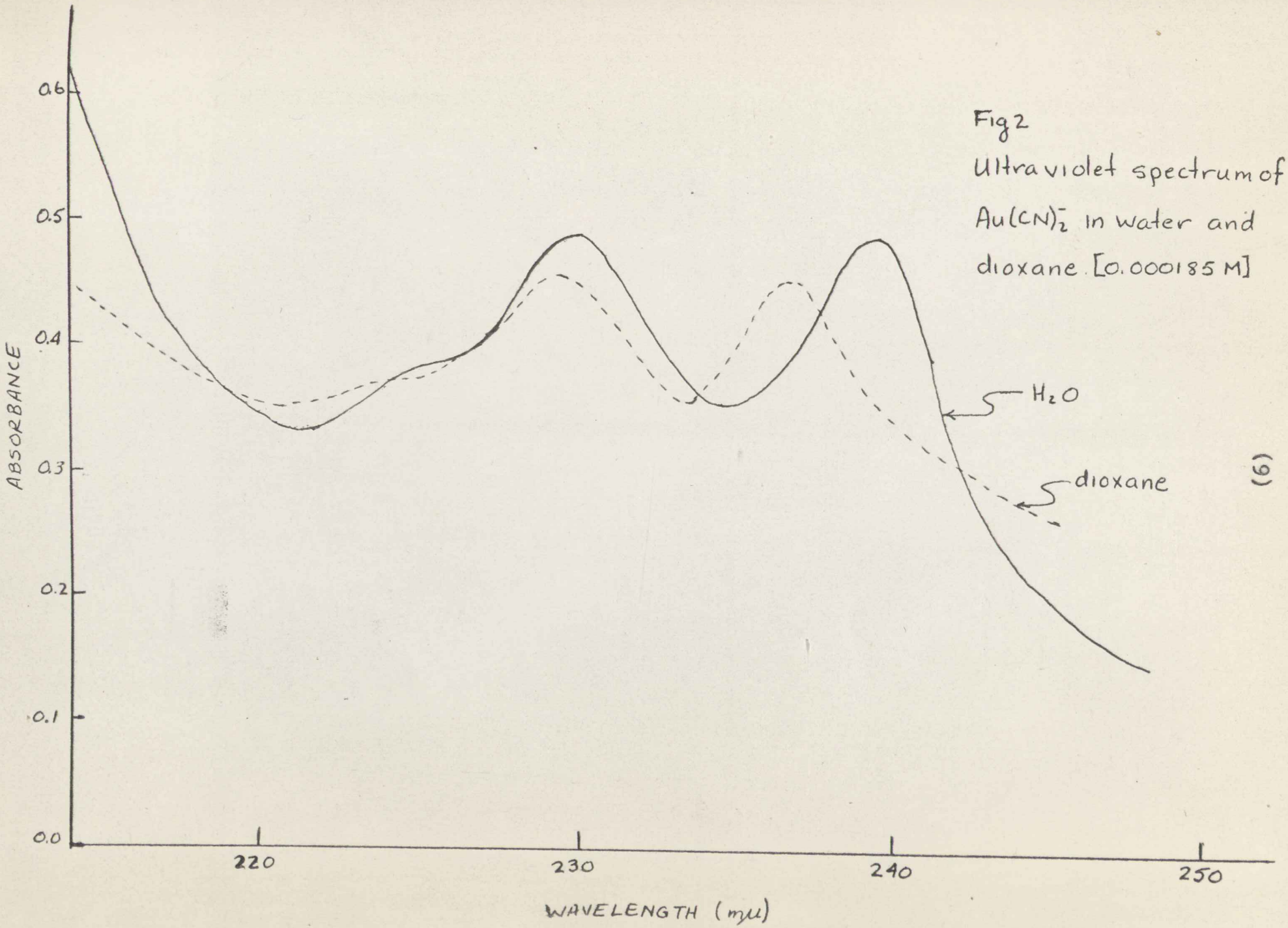


Fig 2
Ultraviolet spectrum of $Au(CN)_2^-$ in water and dioxane. [0.000185 M]